Concepts for a Total Organic Carbon Analyzer for Exploration Missions

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     Monitoring the Total Organic Carbon (TOC) in spacecraft potable water will be of major importance in long-duration human space exploration. In-flight analysis of potable water produced from a regenerative water processor provides immediate feedback on the quality of reclaimed water along with a system health check on the processing hardware. While the International Space Station (ISS) successfully employs a Total Organic Carbon Analyzer (TOCA) to complete these tasks, this device is not configured in a mass and volume form factor most suitable for long-duration missions, nor is it efficiently integrated into the water processing system. This paper summarizes the survey of potential technologies and their feasibility for application in a spaceflight TOC analyzer. The most promising of these technologies have been selected for further evaluation and development with the primary goal to achieve significant reductions in mass, volume, and resupply requirements over the current state-of-the-art TOCA system. Current development is focused on oxidation processes using excimer ultraviolet (UV), photocatalytic UV, or combustion technologies. Carbon dioxide (CO$_2$) detection techniques under development are liquid-phase membrane-transfer conductivity and Raman spectroscopy as well as gas-phase tunable laser spectroscopy. Further work is planned to develop these individual technologies into full-functioning TOC system breadboards followed by selection and advancement to a technology demonstration of a next-generation TOCA on the ISS.

Nomenclature

°C	=	degrees Celsius	*mgC/L*	=	milligrams of carbon per liter
°K	=	degrees Kelvin	*NDIR*	=	non-dispersive infrared
atm	=	atmospheres	*nm*	=	nanometer
C/g	=	carbon per gram	*ppb*	=	parts per billion
ECLSS	=	Environmental Control and Life Support Systems	*ppm*	=	parts per million
			SBIR	=	Small Business Innovation Research
FID	=	flame ionization detector	*SERS*	=	surface-enhanced Raman spectroscopy
GC	=	gas chromatography	*TIC*	=	total inorganic carbon
HCO$_3$	=	bicarbonate	*TiO$_2$*	=	titanium dioxide
ICES	=	International Conference on Environmental Systems	*TLS*	=	tunable laser spectroscopy
			TOC	=	total organic carbon
ISS	=	International Space Station	*TOCA*	=	Total Organic Carbon Analyzer
kg	=	kilogram	*UV*	=	ultraviolet radiation
KHCO$_3$	=	potassium bicarbonate	*µg*	=	microgram
LOD	=	Limit of Detection	*µL*	=	microliter

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I. Introduction

Monitoring the concentration of total organic carbon (TOC) in water is a baseline requirement for maintaining crew health during use of regenerative potable water systems. TOC provides broad-spectrum awareness of product water quality for both toxicity awareness and system health and performance. While the International Space Station (ISS) successfully employs a Total Organic Carbon Analyzer (TOCA)[1] to complete these tasks, this device is not configured in a mass and volume form factor most suitable for long-duration missions. On exploration missions, a TOC analyzer will need to perform potable water analysis reliably and efficiently in a much smaller package than the current ISS TOCA. This paper summarizes a market survey for available systems and technologies that would benefit a spaceflight TOC analyzer and discusses the feasibility of significant reductions in mass, volume, and resupply needs. The most attractive technologies have been selected for further investigation, testing, and maturation. Leading technologies include ultraviolet photo-oxidation and combustion for oxidation of organic chemicals as well as liquid conductivity, tunable diode laser spectroscopy, and Raman spectrometry for CO_2 sensing. The performance of each of these technologies will be discussed as well as integrated device architectures that allow synergy of these technologies.

II. Requirements

A priority in Environmental Control and Life Support Systems (ECLSS) for extended space missions is to recover and process wastewater from condensate and urine to provide potable water for crew consumption and oxygen generation. The TOC concentration indicates the overall quality of reclaimed and stored water and their suitability for crew consumption by indicating the potential presence of hazardous chemicals. For extended missions, water monitoring requires reliable, online sensors, with limited or no need for resupplied chemicals, and a low mass/volume architecture. A challenge to the project is to define requirements for the TOC analyzer even though the mission and vehicle are undefined. Therefore, the current effort is focused on identifying the core system requirements that will determine the technology selection.

The project has proposed a set of requirements including analytical, interface and environmental, safety, and lifetime as the core device requirements. Of these requirements, many are non-discriminating since this is custom design that can be assumed to meet a requirement using understood engineering processes such as design of software controls or design for reliability, maintainability, and generic safety. The less discriminating requirements are not discussed in this paper. For a more detailed review, refer to the 2018 ICES paper for the exploration TOCA[2]. The requirements being used to evaluate technology performance are shown below.

1. Lower detection limit: 0.25 mg/L TOC

The potable water is expected to be < 2 mg/L TOC in a high percentage of samples if the performance is consistent with ISS experience. Consistent insight and trending of TOC can provide health and status of the water recovery system thus providing value even if safely below toxicity limits.

2. Upper detection limit: 10 mg/L TOC

The most significant technology-driving requirement in this list is the upper range for TOC measurement because hazardous chemicals are most commonly used to achieve oxidation of TOC > 2 mg/L. The current toxicology-driven health limit for ISS potable water is 5 mg/L[3]. New toxicology assessments will need to be conducted to evaluate limits for exploration vehicles, so the requirement of 10mg/L provides margin for a relaxed limit as well as some analytical performance above the health limit.

3. Accuracy: +/- 25% from 1 mg/L to 10 mg/L TOC and +/- 0.5 mg/L with <1 mg/L TOC

Accuracy provides confidence in the reported data. This requirement is derived from the ISS TOCA[4] except that ISS does not require accuracy below 1 mg/L TOC. Low-level TOC is less important for crew health or system monitoring since it indicates that all systems are functioning safely. Accuracy and reporting of low-level TOC provides value but could be traded for other performance.

4. Device volume: less than 0.02 m³ (notional)
   Device mass: less than 12 kg (notional)

Device volume and mass are significant drivers of the need for new development of a TOC analyzer. These requirements exclude the current ISS TOCA (0.07 m³ and 36.3 kg), and are smaller than all full-featured commercial TOC analyzers. A size requirement has not been provided as a vehicle interface because vehicle designs are still too

immature. The requirements represent a proposed reasonable improvement assuming new technology selection and packaging.

5. *Power: less than 175 watts average power consumption*

This power consumption requirement is derived from the ISS TOCA[4]. A power limit is difficult to determine at this time since it is too early for power allocations. The proposed limit would require improvement over the existing ISS TOCA. Many technologies can be employed with power consumption well below this requirement. One technology that would be challenged is combustion oxidation.

6. *Lifetime mass/volume should be minimized*

This trade parameter can be helpful in discriminating between options. For the current evaluation mass and volume are being treated collectively since they are often correlated. The primary drivers of the lifetime mass/volume are consumables and maintenance. For example, use of a chemical consumable might simplify the instrument design, but if frequent resupply is needed due to life expiration, then the lifetime mass/volume would be impacted. Likewise, components that require frequent maintenance should not be preferred.

7. *Gravity dependence*

The device must operate in microgravity environment. Most commercial TOC analyzers are gravity dependent, so this requirement is quite excluding. On the other hand, the project has considered a sizable list of potential technologies that have no inherent gravity dependence. All of the currently preferred technology choices are expected to operate independently from gravity especially when the system can be designed for that requirement.

8. *Safety hazards must be controlled*

Safety is always a critical requirement. Technologies that create a hazard are not preferred. Design for hazard control is likely detrimental to mass, volume, complexity, and/or maintainability. Use of hazardous reagents is ruled out for this reason because experience with the original ISS TOCA in 2002 showed that containment levels on the device prevented in-flight maintenance thus ending the unit's life[5]. Control of other hazards like touch temperature may have an acceptable impact and would not rule out a candidate technology.

9. *Maturity/Availability*

Maturity is a subjective assessment of each technology, which is based on potential to meet functional requirements and how well the technology is understood. While this metric would not be included in a device specification, it is a critical parameter for selection of potential design solutions. A theoretical technology may promise to meet all of the desired performance, but if it is not obtainable then it cannot be selected for further development.

III. New Technology Selection Methodology

A multi-phased approach for identification and successive selection of new technology is being employed to narrow the field of possible solutions (Figure 1). The effort began in 2017 with a survey of existing options for TOC analyzers starting with the ISS TOCA. The second phase, conducted in early 2018, was to utilize literature and market publications to identify oxidation and CO_2 detection technologies that could be utilized in a novel TOC analyzer system. These technologies were analyzed against the proposed device requirements to select primary candidates that warrant further investigation. The third phase began in late 2018 and continued into 2019 with a focus on maturation and testing of the preferred technologies in a relevant application. The
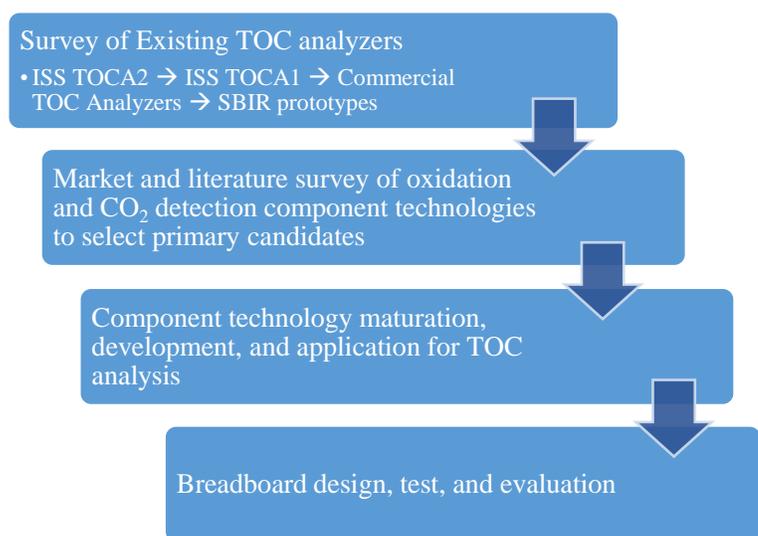

- Survey of Existing TOC analyzers
  - ISS TOCA2 → ISS TOCA1 → Commercial TOC Analyzers → SBIR prototypes
- Market and literature survey of oxidation and CO_2 detection component technologies to select primary candidates
- Component technology maturation, development, and application for TOC analysis
- Breadboard design, test, and evaluation

Figure 1. New Technology Selection Methodology.

second half of 2019 will apply new technologies into breadboard systems for evaluation. The best performing breadboard system will be selected for continuation to a flight technology demonstration.

IV. Survey of Existing TOC Analyzers

Survey of existing hardware reveals that a new system is needed to meet the proposed requirements of an exploration vehicle. The size and maintenance requirements of the current ISS TOCA make it undesirable for the exploration mission requirements. Commercially available TOC analyzers that meet the analytical requirements are large, gravity dependent, and usually require hazardous reagents. Commercial analyzers are available with small size and reagentless, but these instruments are incompatible with the TOC range, ionic composition, and CO_2 content of spaceflight potable water. Previous spaceflight prototypes have been developed under Small Business Innovation Research (SBIR) but these also utilize hazardous chemicals and mercury UV lamps.

V. Component Technology Candidate Assessment

The project performed a research survey of available technologies that could aid in TOC analysis. Many technologies show potential for employment in a TOC analyzer architecture, and further development could yield significant advantages for TOC analysis. As part of the technology assessment, the core functional elements of TOC analysis were identified. These include: (1) oxidation of organic chemicals into carbon dioxide and (2) detection of carbon dioxide. Detection methods are further differentiated as liquid-phase detectors and gas-phase detectors. The following sections outline various technologies that were researched when identifying new techniques for measuring TOC. Because most of the technologies are not ready off the shelf, the technologies were assessed for their potential adaptation to a spaceflight system rather than as an available model. The list is not intended to be exhaustive, but instead captures the sufficient candidates based on usage in industry and in analytical labs as well as technology that shows promise for exploration.

A. Oxidation Technology Assessment

Effective oxidation is essential for TOC analysis. Oxidation converts carbon-based chemicals to carbon dioxide - providing a single analyte for measurement. Table 1 provides a summary of the oxidation techniques that were considered. and their score against the key project requirements, previously discussed in Section II. The scoring system was based on a scale from one to five, with one being least favorable and five being the most. The scores were then weighted, totaled, and expressed as a percentage for comparison purposes. When a value could not be described, e.g., the technology considered too immature, it was assigned value of zero, shown in the table as a "?".

The table is provided because it helps in the consideration of available technologies and the ranking of some of the inherent attributes. However, when considering the technologies for spacecraft applications, the selection to include or exclude was more binary as a function of meeting or not meeting specific criteria. Excluding criteria are shown in the table with red font and a 1 or 2 score. For example, chemical and ozone technologies were ruled out for their inherent hazardous and/or toxicity issues. In addition, chemical addition, by nature, has a large consumable requirement and ozone tends to form bubbles adding the complication of two-phase flow in microgravity. The boron doped diamond (BDD) oxidation technology is attractive as it is the technology currently used in the spacecraft TOCA state-of-the-art. However, the current technology requires a consumable electrolyte/buffer solution. In addition, the ability to shrink the mass and volume requirements of the technology were considered not feasible without moving to new and yet to be proven advanced BDD oxidative processes and/or reactor designs. The ultraviolet (UV) and combustion technologies are particularly attractive in that many conventional TOC analysis are performed using UV-mercury, high temperature and/or catalytic oxidation. When considering spacecraft applications, UV-mercury was ruled out due to toxicity and containment concerns. Similarly, high temperature (1200°C) and catalytic oxidation (650-870°C) systems were ruled out for mass, power, and lifetime limitations. In addition, combustion technologies will likely require additional mass to handle the inherent temperatures and pressures associated with the oxidation process.

Table 1. Oxidation Technology Matrix.

Criteria		LED-UV/ TiO2 catalyst	Mercury UV	Xe Excimer UV (172nm)	Chemical	BDD Electro-chemical	Microfluidic Catalytic Combustion	Advanced BDD Electro-chemical	Commercial TOC Catalytic Combustion	Commerical High Temperature Combustion	Liquid Catalytic Oxidation	Ozone
Additional component list:					*reservoir and dosing system*	*high flow, pressure control, GLS, salt solution*	*heater, zero air supply*		*heater, zero air supply*	*heater, zero air supply*	*heater, oxygen supply, GLS, pressure control*	*oxygen supply, GLS, pressure control*
Oxidation: (oxidize all organic carbon species to CO2)												
Safety		5	2	4	2	5	4	5	4	4	4	3
System Size	Mass	5	5	4	4	2	3	?	1	1	2	2
	Volume	5	5	4	4	2	3	?	2	2	2	2
	Lifetime Mass	5	5	4	2	1	3	?	1	1	2	1
	Power	4	4	4	4	4	3	4	1	1	3	4
Maturity/Availability		3	5	3	5	5	3	1	2	2	1	1
Analytical Requirements		5	2	5	5	5	4	5	4	4	?	?
Life Requirements		5	5	5	5	5	5	5	5	5	5	?
% Performance Score		93%	83%	83%	78%	73%	70%	50%	50%	50%	48%	33%

The UV and combustion oxidation technologies, however, do score high and can meet requirements when emerging technologies are considered. For example, alternative UV sources were considered, including excimer and light-emitting diode (LED) technologies. A xenon excimer lamp emits 172 nm radiation with the capability for direct photolysis of the contaminants and the water molecules[6,7]. Photolysis of water molecules generates strong oxidizing agents in the form of free hydroxyl radicals. The technology offers a good combination of technology readiness, small sample volume, simple operation, and potential for further improvement. Excimer technology was successfully demonstrated in an original Sievers ISS TOCA (1999-2001), however, that system has no commercial demonstration. Like excimer, LED technology capable of reliably generating mid- to near-UV light can be paired with a photo-catalyst to facilitate oxidation without the use of mercury. Here a titanium dioxide catalyst that lowers free energy required to split water into free hydroxyl radicals at the energies emitted by the UV-LED lamps[8,9,10]. For the combustion technology, a miniaturized version of a commercial combustion reactor was considered. The core technology uses a catalyst to lower the required temperature. In addition, the small reactor and accompanying sample size, microliters, results in significantly more favorable energy characteristics. Where high temperature combustion can require hundreds of watts in commercial reactors, the miniaturized device is currently performing at 30 watts.

When comparing the UV and miniaturized combustion technologies, the combustion reactor is expected to have the highest oxidation efficiency, especially at the high range of TOC analysis. At the lower range of TOC analysis, however, combustion systems tend to suffer contamination and/or sample carry-over issues. UV excimer and UV-LED technologies, on the other hand, are expected to perform at least as well as standard TOC systems employing mercury-based UV lamps. With regard to packaging, the UV-LED technology is expected to result in the smallest reactor device - composed of an LED array and a thin film photocatalytic reactor. Using component specifications it is estimated that a photocatalytic reactor could weigh less than 0.25 kg and with a volume less than 500 cm^3 and with less than 10 watt average power draw. UV excimer and combustion reactors are expected to have similar sizing requirements. Excimer technology requires a specific power arrangement and packaging of the xenon gas chamber to achieve 172 nm radiation. Due to the short penetration length of short UV, this technology will also likely require microfluidic applications to efficiently interface the UV energy with the liquid sample. Similarly, the miniaturized combustion reactor, while being only fractions of the size of commercial TOC reactors, will require special packaging considerations for proper thermal protection and insulation. For power consumption, the UV-LED technology is also expected to have the best performance. However, while high temperature combustion can require hundreds of watts for commercial devices, the miniaturized combustion reactor is currently performing at 30 watts or less. Similarly,

excimer lamps for UV generation are expected to require 10 watts or less.

For safety, the UV technologies can be expected have some risk of radiation and the excimer technologies can be expected to generate ozone, if not adequately controlled. Combustion scores lower due to risks of higher temperature and pressure. However, all of the anticipated systems are assumed to be controlled with standard engineering practices. Finally, both the UV and combustion technologies are expected to perform over the entire mission life without maintenance, replacement or need of consumables. This expectation makes lifetime mass a key discriminator in the selection in favor of UV and miniature combustion techniques.

Unfortunately, none of the proposed systems is commercially available. UV-LED is a custom device, but UV-LED arrays are well understood. Deposition of the catalyst coating is not widespread but coating services are commercially available. Excimer lamps that are commercially available do not fit the form factor needed for the project and manufacturing options are limited. A miniaturized combustion reactor is available from Activated Research Company, however, it is designed for gas chromatography processes. Efforts are currently underway to adapt the reactor system to a TOC process.

B. Liquid-phase CO_2 Detection Technology Assessment

As discussed above, following liquid phase sample introduction and oxidation, two potential TOC architectures are possible. The first is CO_2 detection in the liquid phase. A major advantage of making CO_2 measurements directly in the liquid is that the overall analysis remains single phase. For a microgravity system, this architecture is attractive as it has the potential to reduce the overall complexity. The functional requirements dictate that the sensor must be able to detect CO_2 in water down to 0.25 mgC/L and up to at least 10 mgC/L. The sensor must be compatible with potable water quality and must be insensitive to interferences. Table 2 shows the results of the key criteria ranking. The top scorer is direct sample liquid conductivity. This method scores well on almost every metric except that it does not meet the analytical requirements. This method is well characterized by commercial instruments and will report a high bias (up to ~500%) when analyzing chemicals containing ionic components such as calcium, potassium, or chloride. The analytical performance cannot be improved except by modifying to one of the other conductivity implementations, so this option is rejected. The next two highest-ranking options utilize conductivity measurement paired with a CO_2-permeable membrane to account for ionic interference. Conductivity measurement in a deionized water loop was patented and commercialized by Sievers Instruments and remains a leading option in commercial TOC analysis techniques with proven specifications for analytical performance. The maturity/availability rank is not a 5 because the commercial implementation is gravity dependent, and we have not found a commercial vendor that is interested in modifying their design for spaceflight. Some development would be required. Another key factor is the mass and volume required to implement a deionized water loop including a circulation pump, water reservoir, pressure control, and a deionizing system. The commercial deionizer is typically a packed sorbent bed with a limited shelf-life and throughput. Replacement of these deionizers would drive up lifetime mass. An alternative method is being proposed for this project as a hybrid between direct sample conductivity and a deionized water loop. That is removal of CO_2 from the liquid sample using a gas-permeable membrane with conductivity detection located in the liquid sample. With sensors before and after the membrane the loss of CO_2 can be measured with no change in conductivity due to other ions. This technique has not been performed commercially and requires further development. Analytical performance will likely be worse than the deionized water loop but better than direct sample conductivity. A membrane and vacuum pump should sufficiently remove the sample CO_2 that would offer mass and volume savings compared to the deionized water loop system.

Another class of detection systems for direct liquid CO_2 measurement are spectroscopy based. These include Raman spectroscopy, Surface Enhanced Raman Spectroscopy (SERS) and Laser Absorbance Spectroscopy (LAS). Of the three, LAS was ruled out due to insufficient sensitivity unless a high power and mass device was applied. The two Raman approaches are of interest. Raman signal can be obtained either through traditional response or through surface-enhanced Raman spectroscopy (SERS). Both Raman techniques are capable of direct detection of the carbon analyte in the liquid sample with limited interference from other chemicals. Again, direct detection offers simplicity for system implementation. The limitation for Raman spectroscopy is weak signal response for CO_2 species, especially for TOC analysis that requires detection below 1 mgC/L. SERS is designed to enhance the Raman response; however, consumables are required which add to lifetime mass exceeding the project goals. Specific evaluation for this project reveals that commercially available, traditional Raman systems do not meet the detection limit requirement. Various methods are possible for signal enhancement, but each will require increased power, mass, and volume. These enhancements are being investigated, and may be obtainable in a package that meets both analytical and size requirements.

Safety and lifetime are not significant drivers for technology selection since all the options are expected to perform well. The conductivity systems have no identified hazards. The spectroscopy systems are implemented using a laser

that would be contained in the sample exposure area. The conductivity and laser systems are typically specified with operating lifetimes well beyond the project requirements.

Table 2. Liquid-phase CO_2 Detection Technology Matrix.

Criteria		Liquid Conductivity (Direct Sample)	Liquid Conductivity (Membrane Extraction)	Liquid Conductivity (DI Water Loop)	Raman Spectroscopy	SERS	Laser Absorbance Spectroscopy
Additional component list:			*CO_2 permeable membrane*	*CO_2 permeable membrane, water*		*colloid, base, metering system*	
CO_2 Detection in Water Sample: Quantifies CO_2 concentration generated from oxidation and calibrate as TOC. Required Detection Limit < 250 ppb TOC.							
Safety		5	5	5	5	4	5
System Size	**Mass**	5	4	3	3	3	1
	Volume	5	4	3	2	3	1
	Lifetime Mass	5	4	2	3	1	1
	Power	4	4	4	2	4	2
Maturity/Availability		5	3	4	3	2	2
Analytical Requirements		1	3	5	3	3	1
Life Requirements		5	5	5	5	5	5
% Performance Score		**88%**	**80%**	**78%**	**65%**	**63%**	**45%**

C. Gas-phase CO_2 Detection Technology Assessment

In a TOC analyzer, CO_2 generated from oxidation can be detected in the gas phase either through transport across a liquid-to-gas membrane or through complete sample vaporization. The targeted lower detection limit for gas phase measurement cannot be specified as a single number since the requirement will vary depending on the system parameters (carrier gas dilution rate, water sample size, membrane transfer efficiency). Table 3 shows the results of the key criteria ranking of the gas-phase detectors. Ruled out, mostly due to mass, volume, complexity and/or maturity concerns are flame ionization detection (FID), pulsed discharge detector/photo-ionization detection, and thermal conductivity detection. Also not considered was Thermal Conductivity Detection due to sensitivity issues potentially not meeting the analytical requirements. The Tunable Laser Spectrometer (TLS) and non-dispersive infrared (NDIR) detection were the top two performers, respectively. The technologies are similar in that both use infrared absorption to determine CO_2 concentration. TLS has the advantage of probing a spectral region insensitive to water vapor and therefore saves mass and volume associated with gas heating and drying. The TLS optical head is also potentially smaller than the current NDIR used for ISS since it consists simply of a cm-size laser separated several cm from a mm-size detector, with mm-size beam diameter. TLS and NDIR do not require consumables and are projected to meet the device life without maintenance or replacement. Safety controls are not expected to impact hardware design or operation significantly since pressurized gas systems are well understood. TLS and NDIR are expected to meet or exceed the analytical requirements. Both sensors have good heritage, as NDIR has demonstrated analytical performance on the ISS TOCA while a TLS sensor designed by the NASA Jet Propulsion Laboratory has flight heritage from Mars Curiosity TLS. The key advantage of TLS over NDIR is the selection of the 4.3 µm spectral region, allowing CO_2 detection without interference of water vapor. Initial testing of a prototype device has exceeded the requirements for limit of detection and accuracy. The analytical sensitivity of TLS is as good or better than NDIR and insensitivity to water vapor eliminates the need for gas drying components. TLS may even have the capability for operation without a nitrogen carrier gas, further simplifying the implementation. TLS has been selected as the leader for gas-phase CO_2 detection in a compact TOCA system.

Table 3. Gas-phase CO₂ Detection Technology Matrix.

Criteria		Tunable Laser Spectrometer (TLS)	Non-Dispersive Infrared (NDIR)	Thermal Conductivity Detector	Flame Ionization Detector (FID) & Methanizer	Pulse Discharge Detector / Photoionization Detector
Additional component list:		*carrier gas regulator, pressure relief, flow control*	*carrier gas regulator, pressure relief, flow control, heater, dryer*	*carrier gas regulator, pressure relief, flow control, heated GC column*	*carrier gas regulator, pressure relief, flow control, H2 supply bottle/generator, reg., pr.relief, flow control*	*Helium supply bottle, gas regulator, pressure relief, flow control, heated GC column*
CO₂ Detection in Gas: Quantifies CO₂ concentration generated from oxidation and calibrate as TOC.						
Safety		4	4	4	2	3
System Size	**Mass**	4	3	3	1	2
	Volume	4	3	3	1	2
	Lifetime Mass	4	3	3	1	1
	Power	4	3	4	2	3
Maturity/Availability		3	5	3	2	2
Analytical Requirements		5	5	2	5	1
Life Requirements		5	5	5	5	5
% Performance Score		**83%**	**78%**	**68%**	**48%**	**48%**

VI.   Selected Technology Development

   The technology candidates from market and literature research that are deemed feasible to meet requirements and were generally top-scoring were selected for further development. Oxidation technologies that are being pursued are excimer UV, LED-UV photocatalytic, and combustion. For liquid-phase CO₂ detection, development and testing has been conducted for conductivity and Raman technologies. TLS is the only gas-phase CO₂ detector that is selected for development, but NDIR remains a valid backup. All other technologies are not selected for further development. A brief summary of development progress to date is provided in the following sections.

A. Oxidation via Excimer Ultraviolet Lamp

   For in-house development of excimer technology, a UV oxidation reactor (Figure 2) was custom made using a xenon excimer lamp procured from Ushio America, Inc., and a custom spiral wound UV-transparent quartz liquid flow cell. The reactor assembly was housed in a hermetic vessel purged with nitrogen to prevent absorption of the radiation into oxygen and formation of ozone.
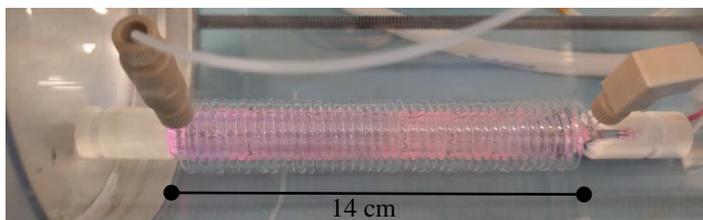

Figure 2. Xenon Excimer Lamp. *172nm, 1mm inner diameter fused silica tube, 6mL volume, 1 ml/min, hermetic chamber at 0.2atm Nitrogen to prevent formation of ozone.*

Testing of the excimer lamp was successful in demonstrating at least 97% TOC reduction for solutions containing 5 to 14ppm TOC (see Figure 3). These results exceed the capability of mercury lamps used without reagents and fully meet the TOC range requirement. Unfortunately, all of the samples maintained a residual TOC of 0.1 – 0.6 mg/L which more significantly affects the lower concentration samples. The samples were performed in triplicate and error bars show the standard deviation. One of the 1 mg/L replicates showed zero TOC reduction. More investigation is needed for certainty, but the residual TOC is believed to be caused by contamination during the process and/or sample handling rather than a lack of oxidative power. More testing is needed to determine best practices and the impact on lower detection limit. In addition to sucrose, the lamp has been tested with successful oxidation of methanol, acetic acid, and dichloromethane.
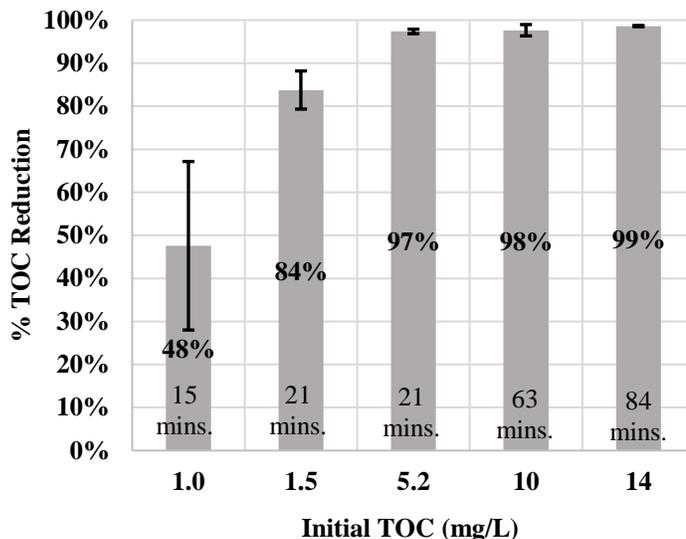
Figure 3. TOC reduction using a 172 nm lamp. *Sample TOC as sucrose was recirculated through a 7mL reactor.*

B. Oxidation via LED Photocatalytic Ultraviolet Lamp

Another alternative to mercury UV lamps is to utilize a UV photocatalytic process that can take advantage of LED technology as the light source. As discussed above, photocatalysis takes advantage of recent advances in LED technology coupled with effectiveness of titanium dioxide (TiO_2) as a photocatalyst in the presence of UV-A light. This technology also lends itself to efficiencies at a microfluidic size with low power draw, and long lifetime, all of which are desired parameters for a spaceflight device. Using component specifications it is estimated that a photocatalytic reactor could weigh less than 0.25 kg and with a volume less than 500 cm^3 and with less than 10 watt average power draw.

For in-house development, a custom reactor (Figure 4) was designed and fabricated for proof of concept testing. Resonance Ltd. of Ontario, Canada designed the device and obtained a catalytic TiO_2 coating from Pureti, Inc. When tested with a known TOC water solution the

Figure 4. LED-UV photocatalytic lamp. *365 nm LED source with titanium dioxide nano-coated flow path.*

device produced low levels of oxidation as measured by downstream conductivity change. Much more efficient oxidation was expected for this device based on other documented research projects. Further evaluation of the device and technology are planned.
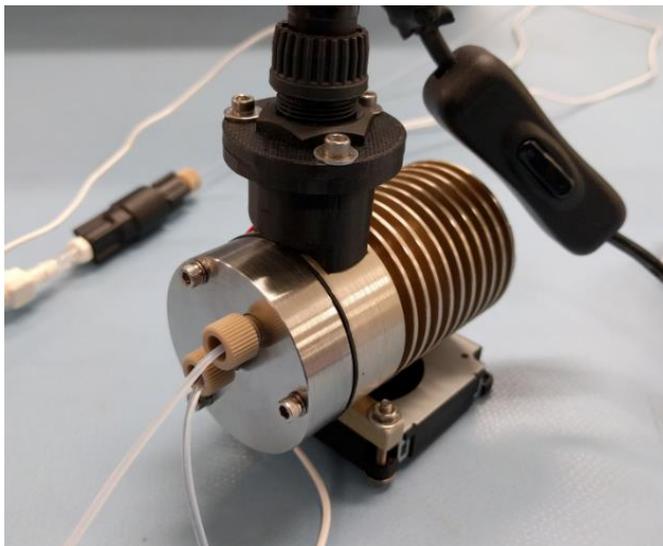
C. Oxidation via Miniaturized Combustion Reactor Development

Combustion of organic chemicals has been proven in commercial TOC analysis; however, market survey demonstrates that commercial combustion reactors do not meet the project requirements due primarily to large size, high power, and high gas consumption. If feasible, a miniaturized combustion reactor would provide benefits in

reduced size, power, and gas consumption, but development and testing are required to advance this technology. For development of a miniaturized combustion reactor, the project identified the Polyarc® reactor provided by Activated Research Company of Eden Prairie, Minnesota. Activated Research Company specializes in catalytic reactors for chromatography processes. Their commercial Polyarc® is the only reactor of its kind that gives users universal carbon response by converting all organic compounds to methane. The form factor for chromatography processes fits the project specifications and sample processing already uses liquid sample injection.

The development goal was to demonstrate proof of concept for miniaturized catalytic oxidation of volatile and non-volatile organic chemicals using modifications to available gas chromatography hardware such as a manual injection inlet and the Polyarc® reactor for total organic carbon measurement in a water system. The primary challenge was to accomplish oxidation of non-volatile organic chemicals since these compounds are typically precipitated in the heated inlet of a chromatography system; however, for TOC analysis, all chemicals must contact the heated catalytic reactor for total combustion.

The basic test setup is shown in Figure 5. The testing utilized a modified Agilent inlet with Helium carrier gas and zero air for oxidation. The water sample was injected using a manual syringe (0.1 μL) for immediate contact and combustion in the 400°C catalytic reactor. The resulting CO_2 was carried with helium and water vapor to a
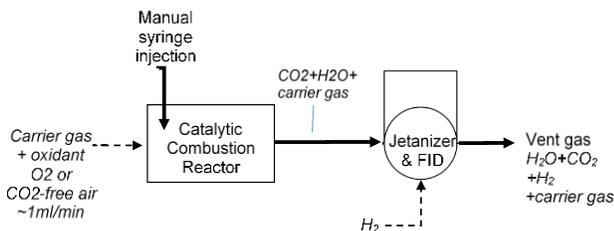

Figure 5. Proof of concept setup for miniaturized catalytic combustion reactor testing for TOC analysis in a water sample using methanizer-FID detection.
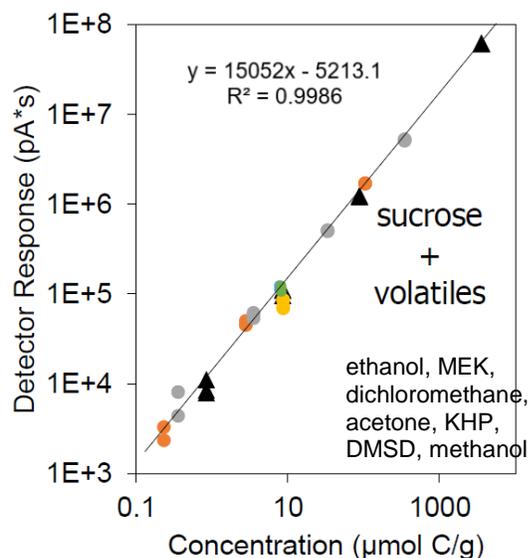

Figure 6. Performance of a miniaturized catalytic combustion reactor for TOC analysis in a water sample.

methanizer and FID for quantification. The system was tested to determine injection limits, limits of detection, and linearity for a variety of test compounds including nonvolatiles and volatiles. The performance is summarized in Figure 6, provided by Activated Research Company.

For a first step, the performance was attractive. The miniaturized reactor demonstrated successful combustion of organic chemicals with equal and linear response for both volatile and non-volatile chemicals. The chemicals tested and shown in Figure 6 include methanol, ethanol, acetic acid, dichloromethane, dimethylsilanediol, potassium hydrogen phthalate, and sucrose. In addition, the combustion occurred at 400°C – notably lower than commercial TOC analyzers and with far lower power requirements related to the reduced mass. As typical for combustion, the oxidation range is extremely high with our testing demonstrating linear performance exceeding 40,000 mgC/L. The challenge for this hardware configuration was at the lower concentrations. Carryover of CO_2 was observed that created a false baseline signal across all samples. With this CO_2 noise the calculated limit of quantification was only 3 mgC/L; however, data analysis suggests that if the CO_2 noise problem was resolved the theoretical limit of quantification would be approximately 0.1 mgC/L thus exceeding the project requirement of 0.25 mgC/L. Further work is ongoing to reduce the CO_2 carryover and test the performance at low TOC concentrations.

D. CO_2 Detection in Liquid-Phase via Conductivity

Liquid phase conductivity is of particular interest to the project. Conductivity is a proven commercial technology, has good sensitivity, linear range, small size, and low power. Three potential configurations for a conductivity sensor have been discussed, direct detection of bicarbonate post-organic oxidation, membrane transfer to a DI loop reference loop, and delta conductivity across a CO_2 membrane extraction. Commercial applications have been established for both the direct and DI configurations. Therefore, although feasibility will be assessed, no technology development

efforts are currently being pursued for these configurations. In addition, the deionized loop is considered the least favorable as it requires additional components that add mass and volume. The alternative approach, CO_2 extracted from the water sample thus creating a measurable decrease in conductivity, is the one where a concerted development effort is underway.

The block diagram of this extraction concept is shown in Figure 7. It borrows from commercial applications but is applied differently. Following oxidation conductivity will rise due to CO_2 generation and dissociation to bicarbonate ions. Membrane extraction of CO_2 lowers the conductivity of the sample water and the conductivity difference can be measured and calibrated to the TOC content. Organic molecules that contain ions like potassium,

Figure 7. Proposed process for conductivity measurement of CO_2 in a water sample.

calcium, or chloride will present a challenge to the detection by increasing the sample conductivity after oxidation; however, the difference in conductivity is proposed to be insensitive to ionic interference since the membrane is only able to remove gaseous CO_2.
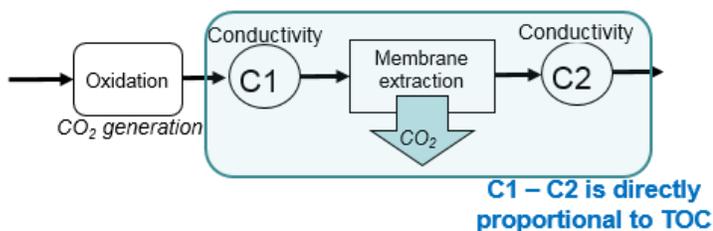
The initial testing goal is to demonstrate measurement of CO_2 content using a CO_2 extraction membrane and delta-conductivity. Carbonated water was used as a sample source. A custom membrane holder was fabricated to hold a 0.45-micron porous hydrophobic membrane. This membrane allows transfer of CO_2 gas through the pores without transfer of liquid water or any other ions. Small, flow-through commercial conductivity sensors (eDAQ) were selected for the testing. Figure 8 shows the results of initial testing. The delta-conductivity was responsive to CO_2 content although higher CO_2 content becomes non-linear possibly due to lack of complete CO_2 transfer. The data also displayed a lack of repeatability in conductivity measurements. This performance may be improved with a better controlled test setup and automation as this was just a first-order test.
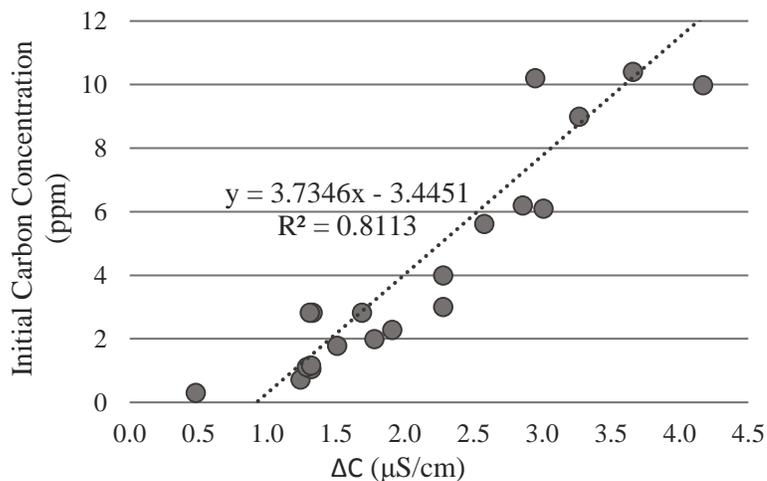

Figure 8. Delta-conductivity measurement of CO_2 in aqueous solution.

E. CO_2 Detection in Gas-Phase via Tunable Laser Spectrometer

Gas phase CO_2 detection in commercial TOC analyzers is commonly performed by NDIR sensors. The ISS TOCA also uses NDIR detection. A challenge for NDIR detection is water vapor interferences since water absorbs at NDIR emitted wavelengths. Gas dryers must be added to remove water. For this project TLS is proposed for gas-phase CO_2 detection. TLS provides much of the same performance as NDIR but with targeted improvements. The first improvement is insensitivity to water vapor. A laser spectral region was selected where water does not absorb; therefore, the gas sample does not have to be dried for accurate measurement. An additional improvement is that the sensor size is smaller than the current ISS TOCA NDIR detector. The device is expected to exceed the project requirements for calibration life and device life.

For Gas phase CO_2 detection, the attributes of the tunable laser spectrometer have been discussed. In short, TLS provides much of the same performance as NDIR but with the potential for several key improvements. The primary advantage is insensitivity to water vapor which eliminates the need to additional gas drying components. Second, the sensor size is smaller than the current ISS TOCA NDIR detector. Finally, TLS is expected to exceed the project requirements for calibration life and device life.

For in-house development, a prototype device was designed and assembled at the NASA Jet Propulsion Laboratory. An Alpes quantum cascade laser at 4284 nm was selected along with a Vigo room-temperature mercury cadmium telluride detector separated by a 7 cm optical pathlength. Refer to Figure 8 for the basic gas-system setup. The prototype was placed in a hermetically sealed chamber to control the environment around the prototype. Testing was conducted using controlled dilution of e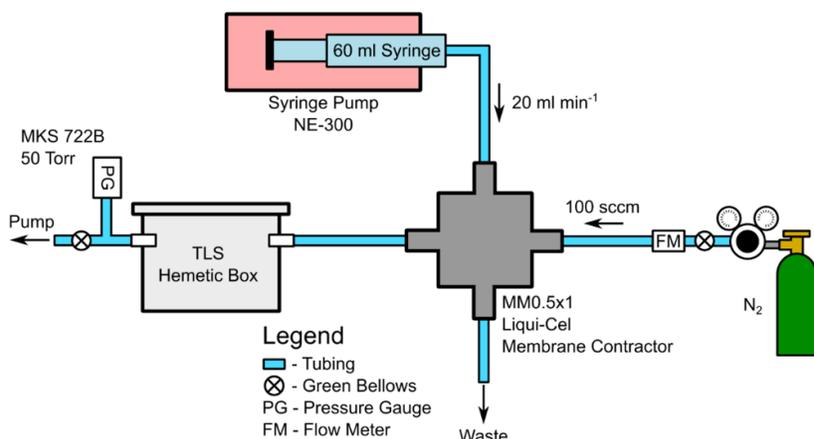ither 1000 or 5.08 ppm CO_2 in N_2 mixtures into pure N_2 with Omega FMA1812 flowmeters (σ 1.5%) and MKS 722 Pressure sensors (σ 0.5%). The TLS was calibrated between 0 and 1000 ppm CO_2; demonstrating good stability and linearity throughout the range. however, the main focus was on concentrations below 5 ppm CO_2 to assess the suitability to the analytical requirements. One goal of the testing was to assess the lower detection limit. In order to accomplish that, measurements were taken at 5 ppm and 2.5 ppm CO_2 by volume with nitrogen, producing an average standard deviation of 0.34 ppm.

With the successful gas-phase testing, the setup was modified to accept water samples containing CO_2 that would allow CO_2 and water vapor to pass across a gas-permeable membrane for detection (Figure 9). This setup is applicable to a liquid oxidation TOCA system, e.g. UV, with membrane transfer to a gas detector. As shown in Figure 10, aqueous samples were prepared at the low range of detection for TOCA – ranging from 0 – 2.6 mgC/L. The test setup was successful in transferring CO_2 from water into the gas measurement system. As expected, the test showed no interference from water vapor. A key observation is that the testing demonstrated an enhancement of CO_2 concentration during transfer from liquid to gas phase of a factor of ~200 under the flow and pressure conditions used. The transfer has a concentrating effect since the gas phase is orders of magnitude lower density than the liquid phase. Note the concentration enhancement as the 2.6 mgC/L sample is detected by the calibrated TLS as 514 ppm CO_2 by volume in the gas phase. The data shows excellent linearity and repeatability even at these very low sample TOC levels. Using the EPA procedure for method detection limit[11], this data set resulted in a detection limit of 0.09 mgC/L thus exceeding the project requirement of 0.25 mgC/L. The testing was a successful demonstration of the detector performance in meeting the requirements for TOC detection limit, upper range, and accuracy. Additional testing is planned to further characterize the performance and identify potential improvements.

Figure 9. Tunable Laser Spectrometer test setup for detection of CO_2 from an acidified inorganic carbon water sample.

mg C(aq) L^{-1}	ppmv CO_2(g)	StDev ($\pm 2\sigma$)	StErr ($\pm 2\sigma$)
0.00	15	1	1
2.60	514	6	1
2.22	424	7	1
1.15	244	3	1
0.82	165	3	1
0.54	123	1	1
0.24	67	2	1
0.23	67	1	1
0.12	51	1	1
0.03	25	1	1

Coefficient values ± one standard deviation
a   =21.113 ± 3.18
b   =186.52 ± 2.68

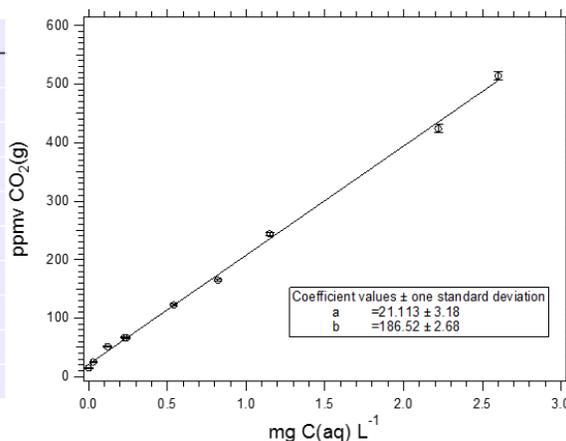**Figure 10. Tunable Laser Spectrometer measurement of CO_2 with membrane transfer from aqueous solution to gas phase. Sweep$_{N2}$ = 100 ml min^{-1}; P $\approx$ 1 atm; Flow$_{H2O}$ = 20 ml min^{-1} liquid; T = 298 °K**

F. CO₂ Detection in Liquid-Phase via Raman Spectrometer

Literature and market search indicate potential advantages of Raman spectroscopy for detection of CO_2. This technology offers direct measurement of CO_2 in the aqueous phase and with selectivity to the specific molecule[12,13]. Most other proposed methods require use of a CO_2 transfer membrane to facilitate detection. Raman spectroscopy also offers a long life instrument with only optical contact with the water stream. Traditional Raman spectroscopy is additionally attractive as it can be performed without use of consumables.

The goal of the early feasibility study for this project was to determine if a Raman or SERS system could be made compatible for measurement of total organic carbon in a water sample through inline aqueous quantification of carbon dioxide and/or bicarbonate (HCO_3-). The compatible system would ideally be small, light, low power, and use few or no consumables. The primary challenge was to determine the lower limit of detection with a system requirement of 0.25 mg/L carbon in water.

Initial testing showed the most attractive sensitivity through use of surface-enhanced Raman spectroscopy (SERS). Characterization testing was performed using gold and silver colloids, varying pH, and 785 nm, 638 nm, and 532 nm excitation wavelengths. A summary of results in shown in Table 4. The best sensitivity was achieved using silver colloids, a pH of 11.5 and 50 mW at 785 nm laser excitation while testing a 50 ppm bicarbonate water solution. This setup produced an estimated limit of detection of 1.4 ppm. Alternatively, the lower wavelength of 532nm produced greater sensitivity than 785 nm when normalized to the power and measurement time applied. The 532nm wavelength performance was adjusted to show the potential for 0.1 ppm limit of detection if power and measurement time were increased to 50 mW and 5 seconds, respectively. However, carbon dioxide does not appear to be SERS active; therefore, this measurement requires the addition of the colloids and a buffer to ensure a pH greater than 8. A summary of the SERS performance is shown in Table 4. In summary, SERS provides attractive sensitivity, yet the mass and volume required for pH adjustment and colloid injection may prove to negate the benefits of SERS spectrometry compared to other detection methods.

Table 4. Comparison of limits of detection for SERS and Raman systems

Laser Wavelength	Limits of Detection (mg/L carbon in water)			
nm	SERS KHCO₃ [1]	SERS KHCO₃ [2]	Raman KHCO₃ [3]	Raman CO₂ [3]
785	0.3	0.2	36	12
638	0.1	0.2	14	not measured
532	0.06	0.01	8	6

Notes:
[1] SERS performance adjusted for 50mW laser power at 5 second exposure; pH 8
[2] SERS performance adjusted for 50mW laser power at 5 second exposure; pH 11.5
[3] Raman performance adjusted for 80mW laser power at 5 second exposure

Traditional Raman spectroscopy was also tested to determine the responsiveness to bicarbonate and CO_2 in water using 785 nm, 683 nm, and 532 nm laser systems. Testing was performed at varying pH and successfully showed the expected equilibrium concentrations of bicarbonate and CO_2 at varying pH as both species were independently quantified. The calculated limits of detection are shown in Table 4. The most relevant data for TOC analysis is direct detection of dissolved CO_2 using traditional Raman systems at 785 and 532 nm. The characteristic Raman response is shown in Figure 11. The best sensitivity for both bicarbonate and CO_2 was achieved using 532 nm laser excitation.
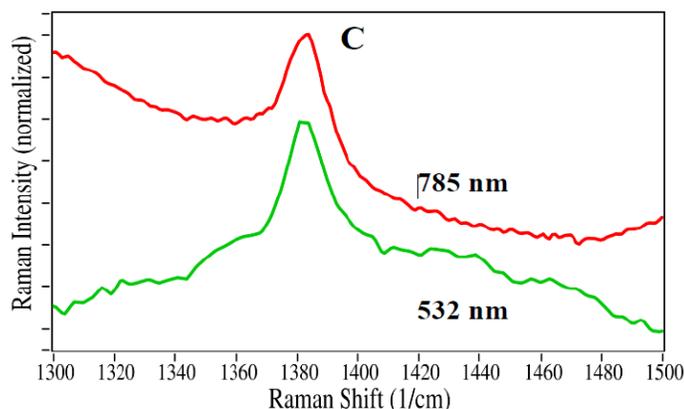

Figure 11. Raman response for water sample containing 1007 ppm carbon dioxide using 80 mW of 785 nm and 1159 ppm carbon dioxide using 50 mW of 532 nm.

This testing demonstrates proof of concept for aqueous quantification of CO_2 through direct optical measurement without use of consumables. The project requirement of 0.25 mg/L carbon has not yet been achieved using traditional Raman spectroscopy. Further work is proposed to increase the limit of detection, by way of (1) increase in excitation power – use of a commercially-available 1500 mW 532 nm laser projected to increase sensitivity by 30x (compared to 50 mW 532 used above), (2) sample cell optical enhancement using multi-pass mirror design projected to increase sensitivity by 3.2x, (3) active cooling of the detector to -10°C projected to increase sensitivity by 5x.Based on the limit of detection of 6 mgC/L for the 532nm laser system compared to the project requirement of 0.25 mgC/L, the technology requires ~24x improvement in sensitivity. A combination of increased laser power, multi-pass optics, and a cooled detector is projected to provide a 480x improvement to exceed the requirement. While a system with these specifications does not currently exist, virtually all of the key components, such as a 1.5W 532 nm laser, do exist. A preliminary design appears possible with modest increase in size, mass, and power. Table 5 shows an estimated comparison of a Raman system against the project requirements. This assessment indicates that a Raman detection system could meet all the key requirements with an optimized assembly, and continued technology development is being considered.

Table 5. Comparison of proposed Raman system to allocated requirements for a TOCA CO_2 detector.

Detector	Mass (kg)	Volume (cm^3)	Power (watts)	LOD (mgC/L)	Lifetime	Consumables	Calibration Frequency
Target Performance	3	5000	50	0.25	10 year	limited	1/year
Raman System (proposed)	~2.5	~3500	<15	~0.03	>10 year	none	~1/year

VII. Conclusion

The ultimate project goal is to demonstrate a flight-capable instrument that meets the proposed functional requirements for long-duration missions. Evaluation of the current ISS TOCA, as well as commercial TOC analyzers, reveals a gap in meeting the proposed exploration requirements. Many new and emerging technologies show potential for employment in a TOC analyzer architecture. Further development of these is anticipated to yield significant advantages for spaceflight TOC analysis. The most promising of these technologies have been selected for further evaluation and development. The current development testing focus is on oxidation processes using UV or combustion and CO_2 detection through membrane-transfer conductivity and Raman spectroscopy in the liquid-phase or tunable laser spectroscopy in the gas phase. These technologies can be utilized in multiple different combinations, but all have the potential for small sample volume, small overall size, zero consumables, long-life, and analytical performance. Under the current multi-year plan, the technologies will be integrated and developed into breadboard systems to develop the system processes and test the performance. Breadboard performance data will be assessed against the project requirements and the best system(s) will be selected for continued work. Ultimately, the project will pursue authorization to design, certify, and deliver a technology demonstration instrument for operation on the International Space Station.

Acknowledgments

References

[1] Clements, A., R. Stinson, and E. Warren, "Development of the Second Generation International Space Station (ISS) Total Organic Carbon Analyzer (TOCA)," *International Conference on Environmental Systems,* SAE: Savannah, GA., 2009.

[2] Morrison, C., S. Schumacher, C. McPhail, M. Callahan, and S. Pensinger, "Considerations on Development of an Exploration Total Organic Carbon Analyzer (TOCA)," *International Conference on Environmental Systems,* Albuquerque, NM., 2018

[3] Ryder, V., "Spacecraft Water Exposure Guidelines (SWEGs)," JSC-63414, 2017

[4] Morrison, C., "Project Technical Requirements Specification (PTRS) for the Environmental Health System (EHS) Total Organic Carbon Analyzer (TOCA) Subsystem," JSC-47212 Rev.C, 2013

[5] Straub, J., et al., "ISS Total Organic Carbon Analyzer Status Update – 2003," *International Conference on Environmental Systems*, SAE: Vancouver, BC., 2003

[6] Mora, A., "UV/Vacuum-UV Advanced Oxidation Process for the Treatment of Micropollutants from Drinking Water Sources Under Common Operation Temperatures," *The University of British Columbia: Open Collections* [online database], URL: https://open.library.ubc.ca/cIRcle/collections/ubctheses/24/items/1.0228628 [cited 28 March 2018].

[7] Stefan, Miheala, *Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications*, IWA Publishing, 2018, 686 pages

[8] Wang, N., "Microfluidic reactors for photocatalytic water purification," *Lab Chip*, Issue 6, 2014, pp1074-1082

[9] W.-K. Jo, R.J. Tayade, "New Generation Energy-Efficient Light Source for Photocatalysis: LEDs for Environmental Applications", *Ind. Eng. Chem. Res*., 21 Jan 2014, Vol. 53, No. 6, pp. 2073−2084.

[10] Sergejevs, A., "A calibrated UV-LED based light source for water purification and characterization of photocatalysis," *Photochem. Photobiol. Sci*., Issue 11, 16 Oct 2017, pp. 1690–1699

[11] "Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11", 40 CFR Appendix B to Part 136, 2011

[12] Achwarzwelder, A., "Raman spectroscopy of the CO2-H2O System", Master's Thesis, Ohio State University, pg 37-39, 2006.

[13] White, S.N., "Qualitative and quantitative analysis of CO2 and CH4 dissolved in water and seawater using laser Raman spectroscopy". *Applied spectroscopy*, 64(7*)*, 2010, pp.819-827